Wastewater Treatment with Magnetic Separation

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CRADA with DuPont established June 17, 2002

FY2003 Project Funding: $ 60 k (DOE)
$150 k (DuPont funds-in)
$100 k (DuPont in-kind)

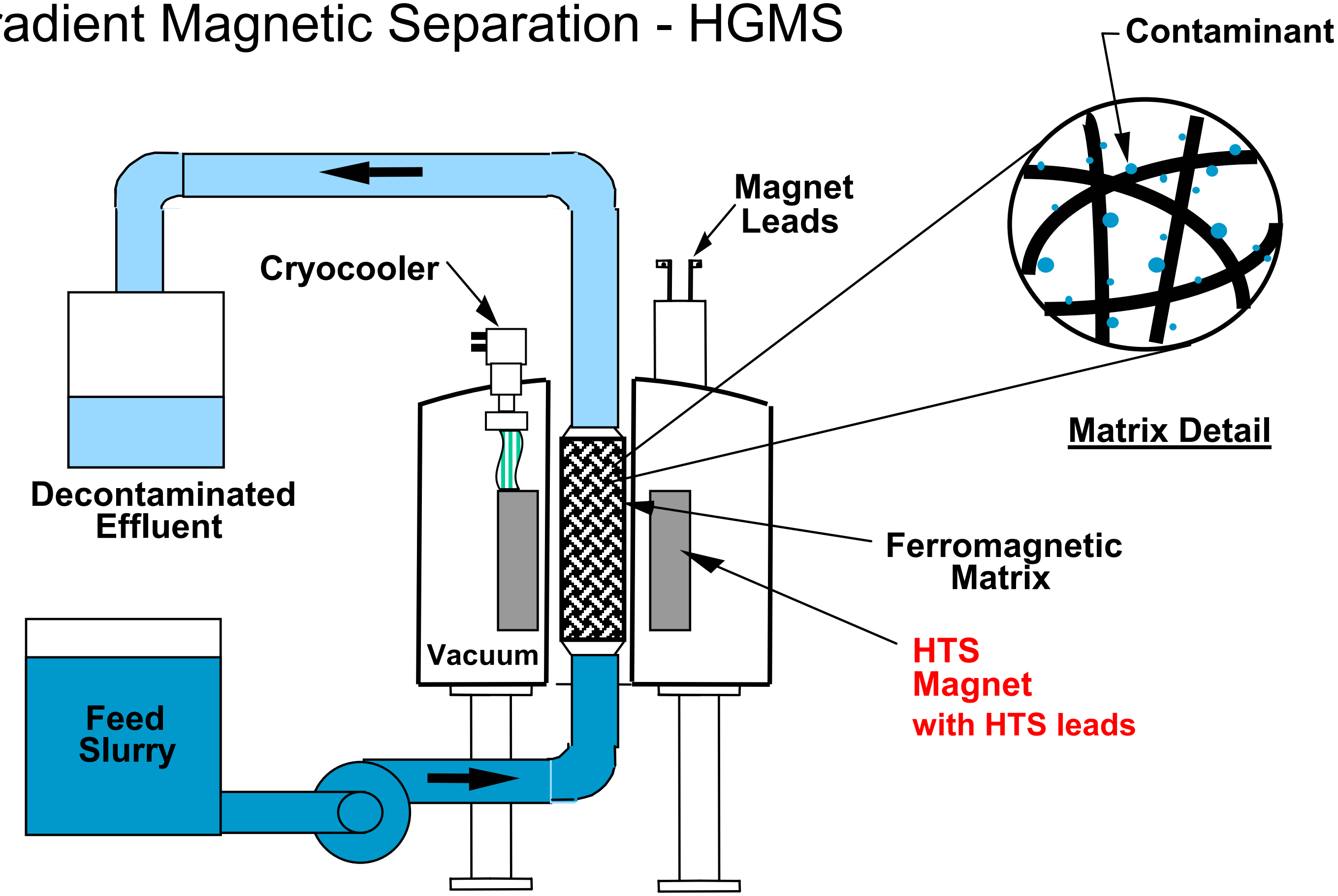
2003 DOE Annual Peer Review
Washington, DC July 23-25, 2003

Outline

- Overview of HTS Magnetic Separation
- Research Integration
- FY 2003 Results
- FY 2003 Performance
- FY 2004 Plans

Overview - What is Magnetic Separation?

High Gradient Magnetic Separation - HGMS



Overview - Why Magnetic Separation?

- Very efficient removal of magnetic particles *(kaolin clay, TiO_2)*
- Clever chemistry to magnetically capture target molecules
- New market applications - *wastewater treatment, water purification, medical/biological separations, capture target compound*
- Potential near term success - *heavy metal removal from mine drainage*
  - 1000's of mines with heavy metal drainage issues
  - significant market opportunity if cost effective

Overview - Why HTS Magnetic Separation?

- Reduced electrical usage compared to resistive coil technology
- Can be portable with cryogen-free magnet *(important for temporary cleanup or remote site)*
- Smaller footprint than more conventional technologies- *potentially less expensive because less real estate*
- Fewer chemicals (safer) - *ferrite process vs. conventional precipitation technique*
- Environmentally friendly - *ferrite process produces non-hazardous, non-leachable waste*
- Cheaper to dispose of waste

Overview - Magnetic Separation SPI Program

- HTS magnetic separator offers significant operational energy savings
- DuPont business plan calls for development of new applications of HGMS that benefit from energy savings
- DuPont capitalizing on LANL's 10 years experience in magnetic separation:
  - process development
  - HTS magnetic separation equipment
  - chemical analytical equipment/expertise
  - multi-disciplinary approach
    - chemists, chemical engineers, magnetics, SC, modeling

Research Integration

- Regular technical interchanges with DuPont, Wilmington
- Collaboration with New Mexico State University
- Jon Bernard, DuPont employee
  - Stationed full-time at LANL
  - fully equipped laboratory at LANL Research Park
  - integrated into LANL magnetic separation team
  - access to LANL analytical equipment & expertise

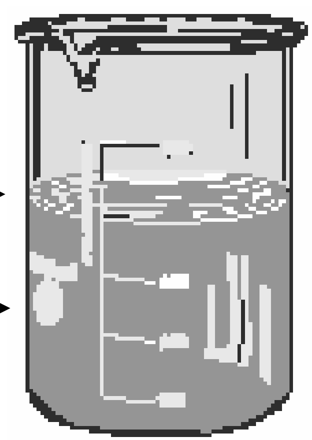
HGMS
A Two-Step Process

Step 1 – Synthesis of slurry

Step 2 – HGMS (high gradient magnetic separation

Wastewater

Chemicals



Magnetic Separator

Cleaned water

Separator backflush

Solid/liquid separation

Solid/sludge

- Cleaned water is released to the environment
- Sludge is disposed of in a landfill

Step 1 - Magnetite Formation

<u>Step 1</u> – Formation of Green Rust (GR)

$Fe^{2+} + 2\ Fe^{3+} + 8\ OH^{-} \rightarrow GR\ (solid)$

<u>Step 2</u> – Dehydration to form magnetite

$GR\ (solid) \rightarrow FeOFe_2O_3\ (solid) + 4\ H_2O$

- $FeOFe_2O_3$ normally written as Fe_3O_4
- 1 Fe^{2+} : 2 Fe^{3+} stoichiometry necessary
- GR forms readily but has a <u>low magnetic susceptibility</u> and is <u>air (O_2) sensitive</u>
- Dehydration is the Rate Determining Step (RDS)

Formation of Metal Substituted Magnetite

$$M^{2+} + 2\,Fe^{3+} + 8\,OH^{-} \rightleftarrows MO{\bullet}Fe_2O_3\ (\text{solid}) + 4\,H_2O$$

<u>or</u>

$$Fe^{2+} + Fe^{3+} + M^{3+} + 8\,OH^{-} \rightleftarrows FeO{\bullet}FeMO_3\ (\text{solid}) + 4\,H_2O$$

- M = Metal (ie. Cu^{2+}, Mn^{2+}, Cd^{2+}, Pb^{2+}, Ag^{+}, As^{3+}, etc.)
- Substituted magnetite = <u>**Ferrite**</u>

Selection of a Method to Synthesize Magnetite/Ferrite

In-situ aerial oxidation:

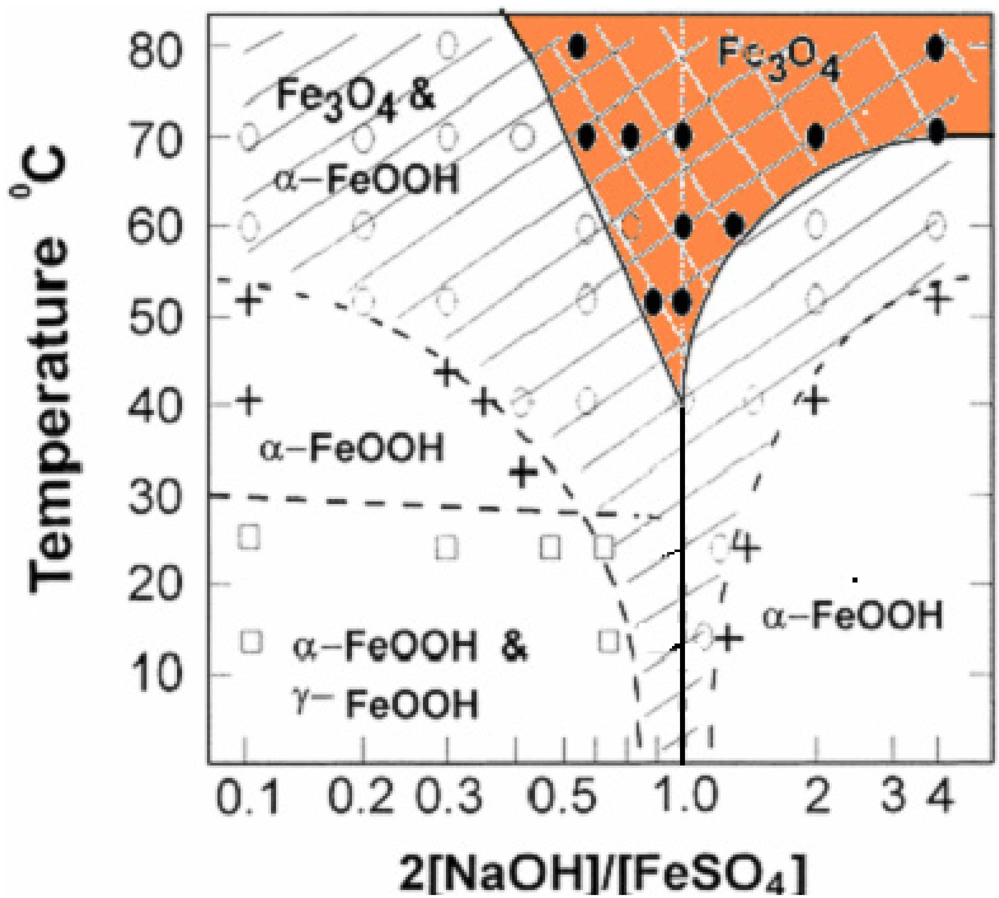
- Produces consistently high quality ferrite

$$FeSO_4\ (\text{solid}) \rightarrow Fe^{2+}$$

$$Fe^{2+} + 2OH^- \leftrightarrows Fe(OH)_2\ (\text{solid})$$

$$6\ Fe(OH)_2\ (\text{solid}) + O_2\ (\text{air}) \rightarrow 2\ Fe_3O_4\ (\text{solid}) + 6\ H_2O$$

Magnetite Phase Diagram

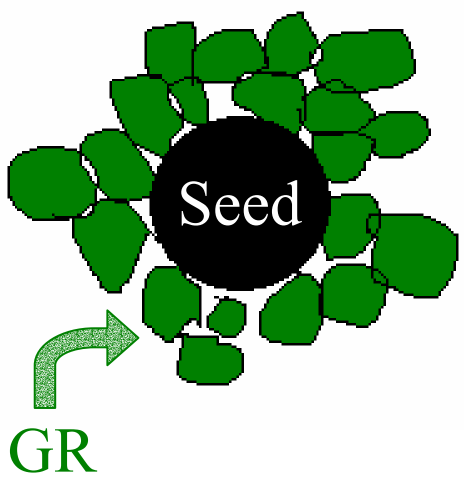


Kiyama, *M. Bull. Chem. Soc. Jpn*. **1974**, 47 1646-1650.

- Difficult to form magnetite below 40ºC

Our Approach – Magnetic Seeding

Magnetic seeding – A template effect:



- Produces a suitably magnetic particle
- Allows for magnetic separation
- Green rust can be dealt with post-magnetic separation

Step 1 – Experimental Details

1. Take a sample of wastewater and stir
2. Add magnetite seed and disperse
3. Add Fe^{2+} and dissolve
4. Add NaOH to pH ~ 10
5. Bubble air through suspension for 15 min
6. Can filter to sample solid phase or "cleaned" water for analysis

Wastewater + seed

Green Rust/Seed particles after reaction

FY03 Results
Magnetite Seeding Experiments

The experiments:

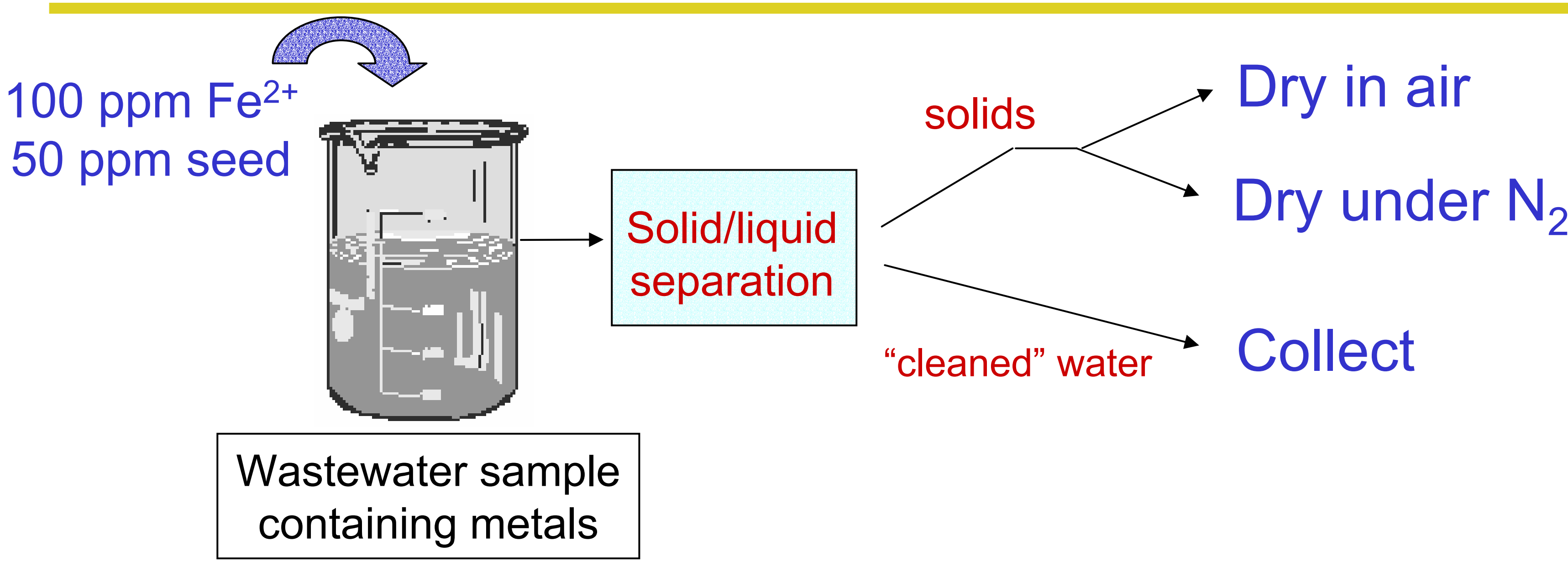
1. 50 ppm seed, 50-1000 ppm Fe^{2+}

2. 50 ppm Fe^{2+}, 50-250 ppm seed

Key findings:

- Seed/GR particle forms with good magnetic response
- Particles suitable for magnetic separation
  - Will allow GR to ferrite conversion after solid/liquid separation

Product Analysis: Converting Green Rust to Ferrite



Solids:
- XRD (X-ray diffraction)
- TCLP test (toxicity characteristic leaching protocol)

Liquid:
- ICP-AES (inductively coupled plasma – atomic emission spectroscopy)

FY03 Results
Conversion of Green Rust to Ferrite - Analysis

XRD:

• Magnetite/ferrite present only in the product dried under nitrogen

TCLP:

• Product dried under nitrogen passes TCLP test

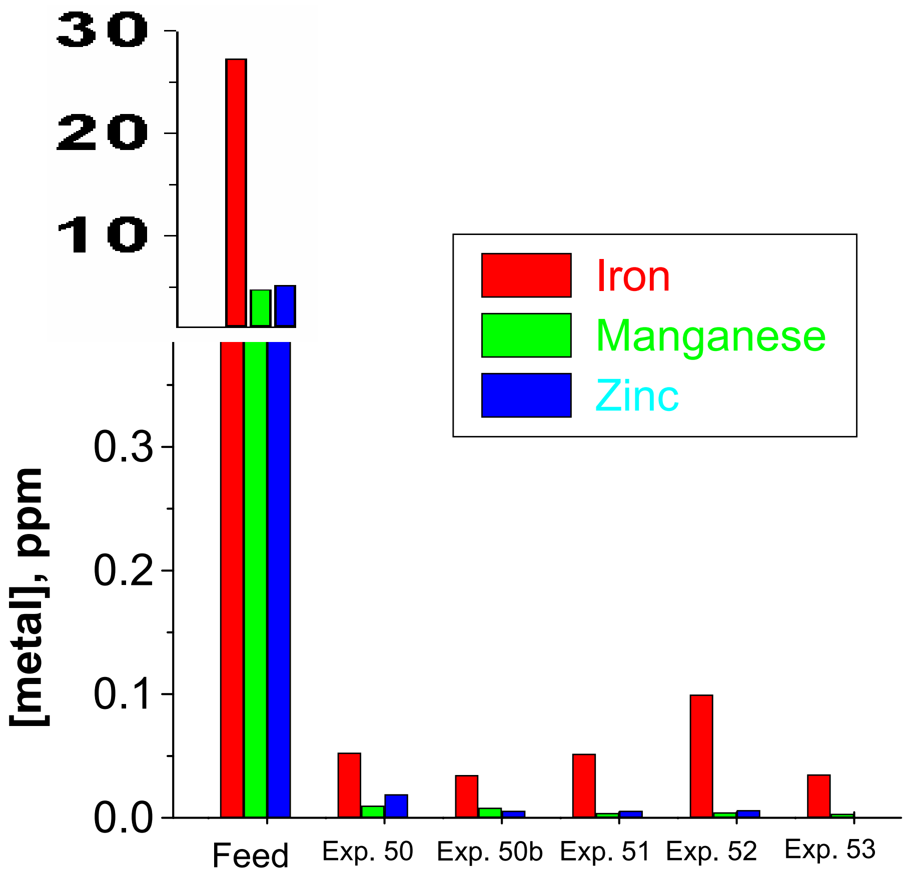
Findings:

• GR to ferrite conversion is viable after magnetic separation

• Ferrite stability allows for inexpensive disposal in a non-hazardous waste landfill

FY03 Results

Does Ferrite Synthesis Remove Typical Metals?



- Initial metal concentrations of 1-30 ppm
- Representative metals chosen (non RCRA)

RCRA = Resource conservation and Recovery Act

- Also works for heavy metals of <u>current</u> interest such as arsenic, lead and cadmium

- Residual concentrations meet NPDES limits for discharge (NPDES = National Pollution Discharge and Elimination System)

Magnetic Separation – Step 2

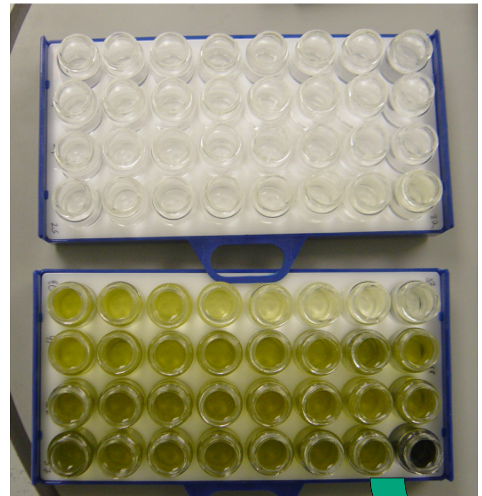
FY03 Results
HTS Magnet

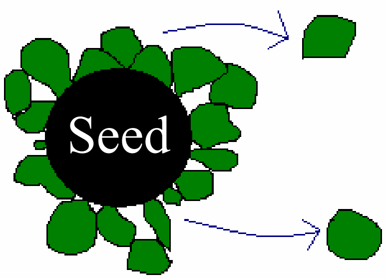
- 624 m of Bi-2223/Ag superconducting tape
- Overall coil dimensions of 18 cm OD, 15.5 cm height and 5 cm ID
- Cooled by a two stage Gifford-McMahon cryocooler
- At 40 K the magnet can generate a central field of 2.0 T at a current of 120 A

FY03 Results
Particulate Breakthrough

Seed/GR particle

HGMS



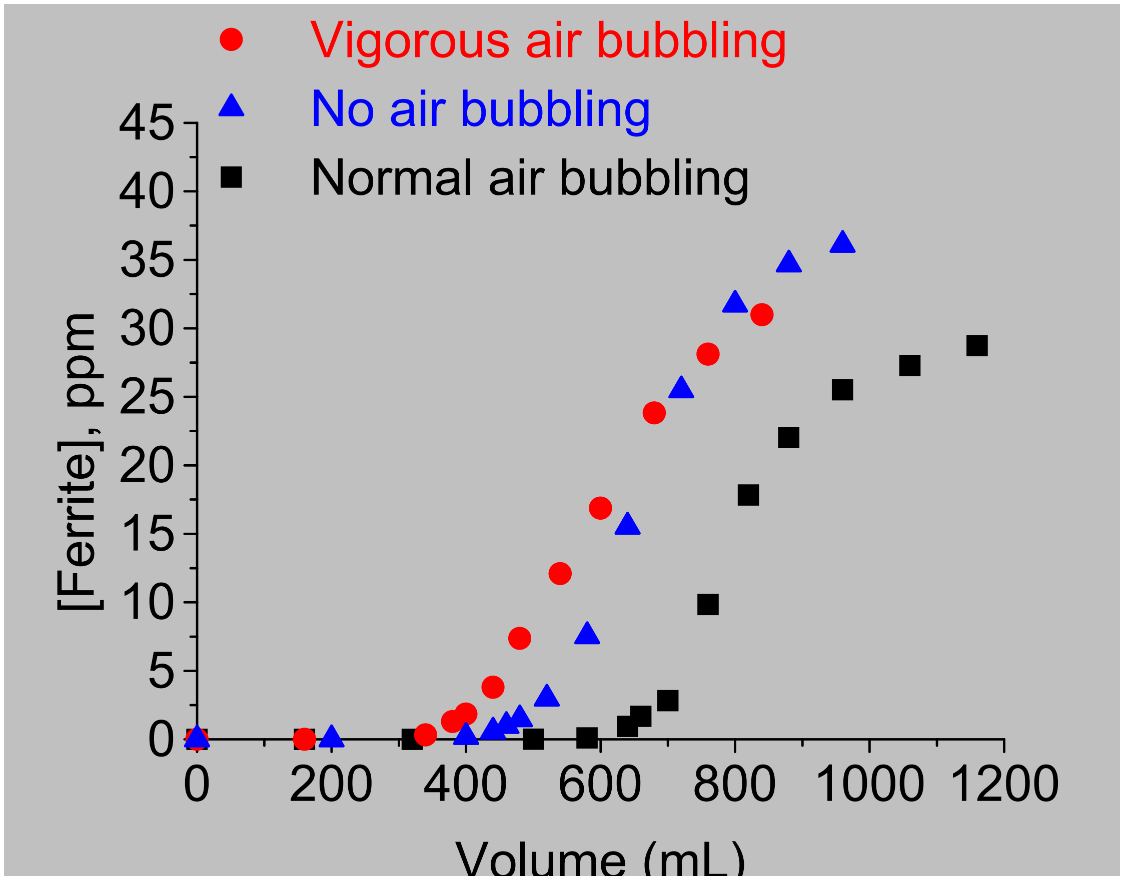


- Breakthrough concentrations measured using a turbidimeter
  - Breakthrough defined as <u>1 ppm</u>
- Seed readily trapped in separator
- GR shears from seed
- Increasing seed/GR stability should increase breakthrough volumes

There are Numerous Separator Performance Variables to be Addressed

- Particle size
- Particle concentrations
- Wastewater pH
- Type of stainless steel wool (ultra-fine to coarse)
- Applied magnetic field strength
- Flow velocity in column
- Residence time in the column

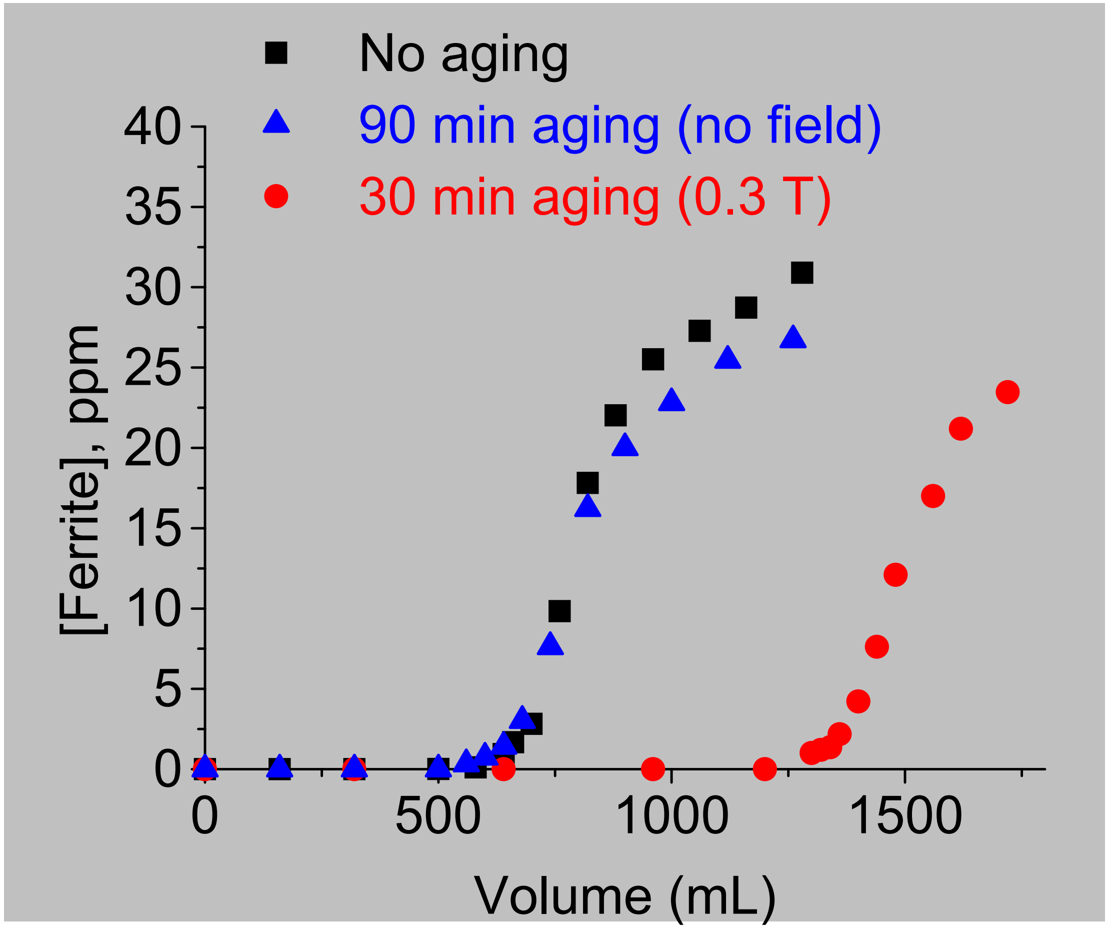
FY03 Results
Effect of the Rate of Air Bubbling During Synthesis



Conclusions

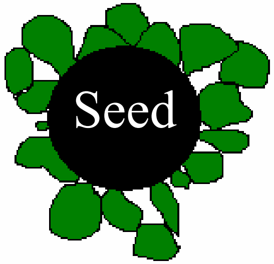
- Need to control rate of air bubbling
- Influences “quality” of seed/GR particle in step 1

FY03 Results
Effect of Aging in a Magnetic Field Prior to HGMS

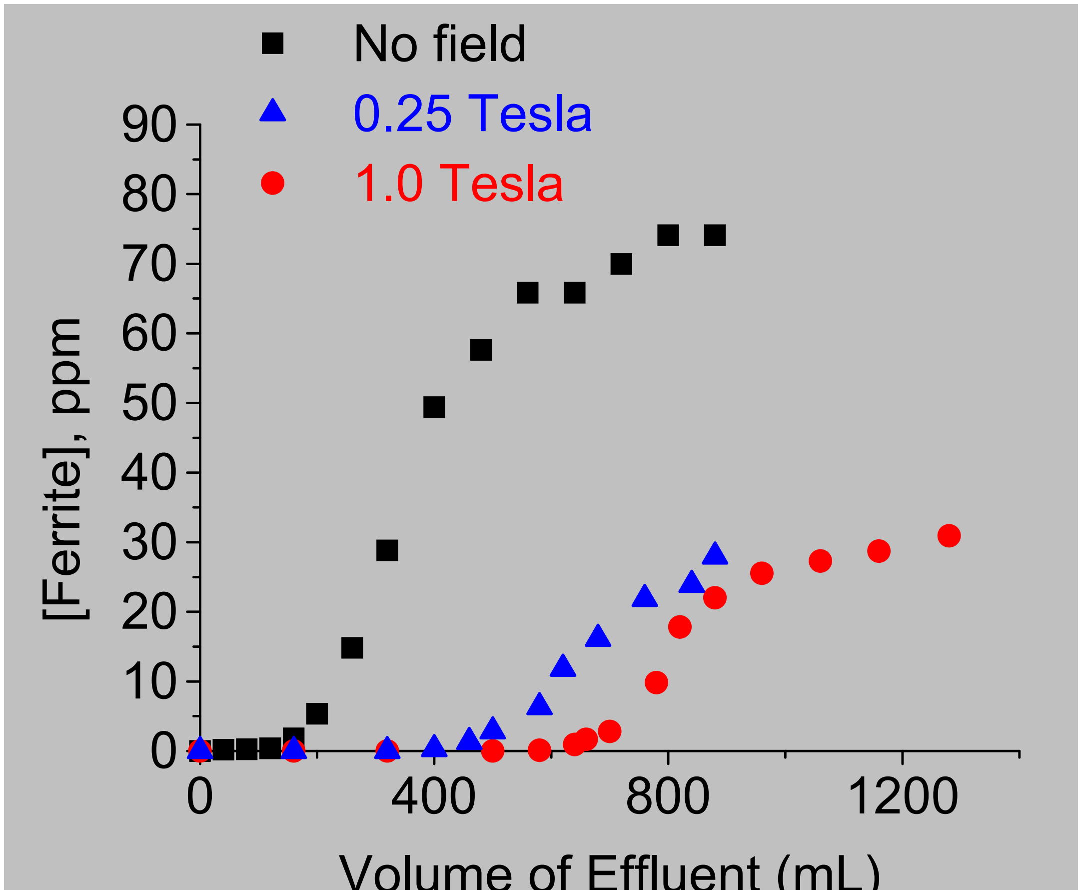


Conclusions:

- Aging in a magnetic field dramatically increases breakthrough volume
- Magnetic aging increases the stability of the seed/GR particle



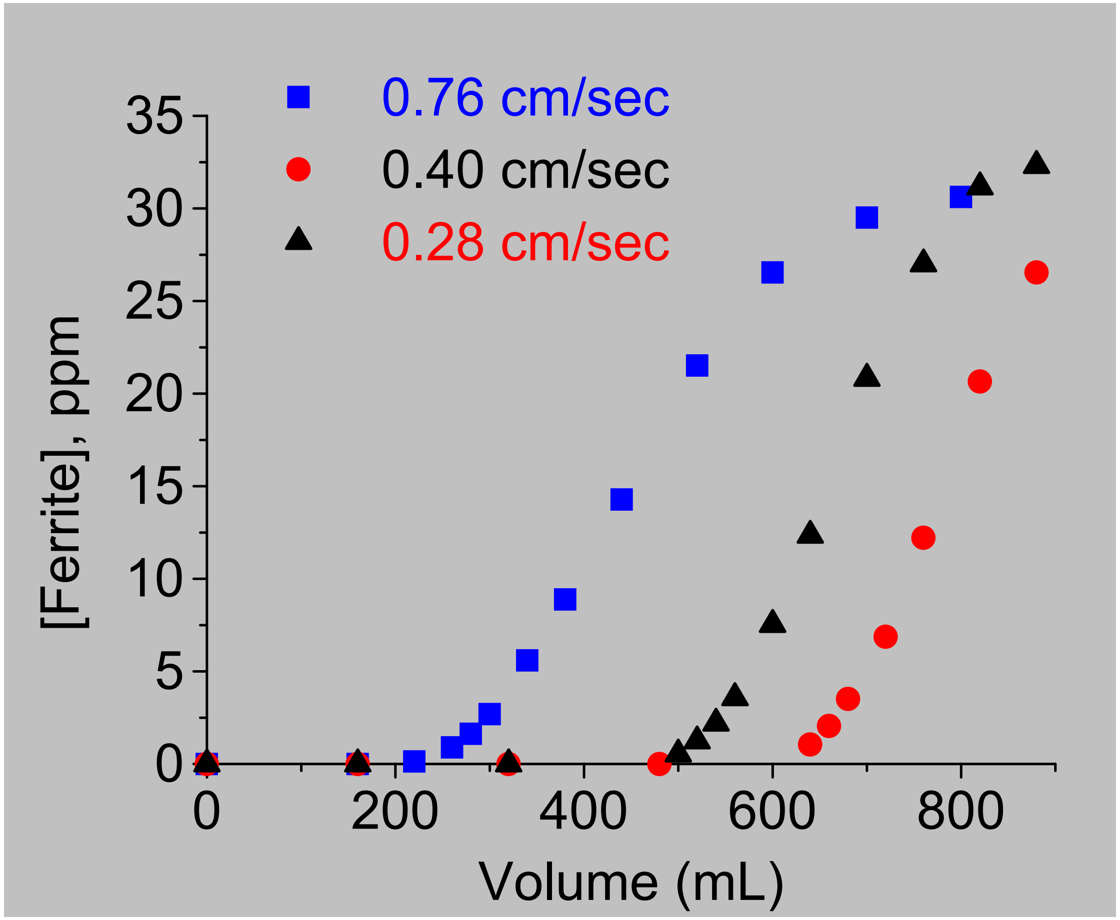
FY03 Results
Effect of Applied Field



Conclusions:

- Higher field strengths result in larger magnetic forces
- Larger breakthrough volumes at higher field

FY03 Results
Effect of Flow Velocity in the Column



Conclusions:

• Breakthrough volume increases with decreasing flow velocity in the column

• But: Process takes longer

FY03 Results
Summary

Step 1: Synthesis

• Metals can be removed from wastewater using our ferrite synthetic procedure
• Effluent water can be released to the environment
• Ferrites are environmentally stable and can be disposed of inexpensively

Step 2: HGMS

• Our seeded ferrite process allows us to do a magnetic separation prior to green rust conversion to ferrite

FY03 Performance CRADA Tasks/Deliverables

All CRADA deliverables have been met

- ✓ CRADA established 6/17/2002
- ✓ Jon Bernard hired
- ✓ Lab & office established/equipped in Research Park
- ✓ Determined area/market of focus (CRADA deliverable - report)
- ✓ Established feasibility of low temperature ferrite process (CRADA deliverable - report)
- ✓ Optimizing HTS process – as per CRADA plan

FY04 Plans
CRADA Tasks/Deliverables

- Determine controlling parameters and ranges for ferrite process - step 1 *(parameter sensitivity evaluation)*
- Optimize ferrite & HGMS processes *(optimize process for specific application/site, determine how process variables might change for different conditions/application)*
- Determine scaling issues from laboratory to pilot plant *(quantities of chemicals, processing times, equipment cost)*
- Establish pilot plant partner *(demonstrate the technology in the field)*